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2,324,699, on October 27, 2000, by **QUESTAIR TECHNOLOGIES INC.**, assignee of
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CARBON MONOXIDE REMOVAL FROM HYDROGEN FEED TO FUEL CELL

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FIELD OF THE INVENTION

The present invention relates to a fuel cell-based electrical generation system which employs pressure swing adsorption for enhancing the efficiency and durability of the fuel cell.

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BACKGROUND OF THE INVENTION

Fuel cells provide an environmentally friendly source of electrical current. One form of fuel cell used for generating electrical power, particularly for vehicle propulsion and for smaller scale stationary power generation, includes an anode channel for receiving a flow of hydrogen gas, a cathode channel for receiving a flow of oxygen gas, and a polymer electrolyte membrane (PEM) which separates the anode channel from the cathode channel. Oxygen gas which enters the cathode reacts with hydrogen ions which cross the electrolyte to generate a flow of electrons. Environmentally safe water vapour is also produced as a byproduct.

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External production, purification, dispensing and storage of hydrogen (either as compressed gas or cryogenic liquid) requires costly infrastructure, while storage of hydrogen fuel on vehicles presents considerable technical and economic barriers. Accordingly, for stationary power generation, it is preferred to generate hydrogen from natural gas by steam reforming or partial oxidation followed by water gas shift. For fuel cell vehicles using a liquid fuel, it is preferred to generate hydrogen from methanol by steam reforming or from gasoline by partial oxidation or autothermal reforming, again followed by water gas shift. However, the resulting hydrogen contains carbon monoxide and carbon dioxide impurities which cannot be tolerated respectively by the PEM fuel cell catalytic electrodes in more than trace levels.

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The conventional method of removing residual carbon monoxide from the hydrogen feed to PEM fuel cells has been catalytic selective oxidation, which compromises efficiency as both the carbon monoxide and a fraction of the hydrogen are consumed by low temperature oxidation, without any recovery of the heat of combustion. Palladium diffusion membranes can be used for hydrogen purification, but have the disadvantages of delivery of the purified hydrogen at low pressure, and also the use of rare and costly materials.

Pressure swing adsorption systems (PSA) have the attractive features of being able to provide continuous sources of oxygen and hydrogen gas, without significant contaminant levels. PSA systems and vacuum pressure swing adsorption systems (VPSA) separate gas fractions from a gas mixture by coordinating pressure cycling and flow reversals over an adsorber or adsorbent bed which preferentially adsorbs a more readily adsorbed gas component relative to a less readily adsorbed gas component of the mixture. The total pressure of the gas mixture in the adsorber is elevated while the gas mixture is flowing through the adsorber from a first end to a second end thereof, and is reduced while the gas mixture is flowing through the adsorbent from the second end back to the first end. As the PSA cycle is repeated, the less readily adsorbed component is concentrated adjacent the second end of the adsorber, while the more readily adsorbed component is concentrated adjacent the first end of the adsorber. As a result, a "light" product (a gas fraction depleted in the more readily adsorbed component and enriched in the less readily adsorbed component) is delivered from the second end of the adsorber, and a "heavy" product (a gas fraction enriched in the more strongly adsorbed component) is exhausted from the first end of the adsorber.

However, the conventional system for implementing pressure swing adsorption or vacuum pressure swing adsorption uses two or more stationary adsorbers in parallel, with directional valving at each end of each adsorber to connect the adsorbers in alternating sequence to pressure sources and sinks. This system is often cumbersome and expensive to implement due to the large size of

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the adsorbers and the complexity of the valving required. Further, the conventional PSA system makes inefficient use of applied energy because of irreversible gas expansion steps as adsorbers are cyclically pressurized and depressurized within the PSA process. Conventional PSA systems could not be applied to fuel cell power plants for vehicles, as such PSA systems are far too bulky and heavy because of their low cycle frequency and consequently large adsorbent inventory.

SUMMARY OF THE INVENTION

According to the invention, there is provided a fuel cell based electrical generation system which addresses the deficiencies of the prior art fuel cell electrical generation systems, particularly as to purification of reformat hydrogen.

The electrical current generating system comprises a fuel cell, an oxygen gas delivery system, and a hydrogen gas delivery system. The fuel cell includes an anode channel having an anode gas inlet for receiving a supply of hydrogen gas, a cathode channel having a cathode gas inlet and a cathode gas outlet, and an electrolyte in communication with the anode and cathode channel for facilitating ion transport between the anode and cathode channel. The oxygen gas delivery system is coupled to the cathode gas inlet and delivers air or oxygen (e.g. oxygen enriched air) to the cathode channel.

The oxygen gas delivery system may simply be a air blower. However, for superior performance it incorporates an oxygen pressure swing adsorption system, including a rotary module having a stator and a rotor rotatable relative to the stator, for enriching oxygen gas from air. The rotor includes a number of flow paths for receiving adsorbent material therein for preferentially adsorbing a first gas component in response to increasing pressure in the flow paths relative to a second gas component. The pressure swing adsorption system also may include compression machinery coupled to the rotary module for facilitating gas flow through the flow paths for separating the first gas component from the second gas

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component. The stator includes a first stator valve surface, a second stator valve surface, and plurality of function compartments opening into the stator valve surfaces. The function compartments include a gas feed compartment, a light reflux exit compartment and a light reflux return compartment.

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In one variation, the compression machinery comprises a compressor for delivering pressurized air to the gas feed compartment, and a light reflux expander coupled between the light reflux exit compartment and the light reflux return compartment. The gas recirculating means comprises a compressor coupled to the light reflux expander for supplying oxygen gas, exhausted from the cathode gas outlet, under pressure to the cathode gas inlet. As a result, energy recovered from the pressure swing adsorption system can be applied to boost the pressure of oxygen gas delivered to the cathode gas inlet.

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The oxygen gas delivery system is coupled to the cathode gas inlet and delivers oxygen gas to the cathode channel. The hydrogen gas delivery system supplies purified hydrogen gas to the anode gas inlet, and may have provision for recirculating hydrogen gas from the anode gas exit back to the anode gas inlet with increased purity so as to avoid accumulation of impurities in the anode channel.

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In a preferred embodiment, the oxygen gas separation system comprises an oxygen pressure swing adsorption system, and the hydrogen gas separation system comprises a reactor for producing a first hydrogen gas feed from hydrocarbon fuel, and a hydrogen pressure swing adsorption system coupled to the reactor for purifying hydrogen gas received from the first hydrogen gas feed. Hydrogen gas from the anode exit may be recirculated to the hydrogen pressure swing adsorption system as a second hydrogen gas feed. Both pressure swing adsorption systems include a rotary module having a stator and a rotor rotatable relative to the stator. The rotor includes a number of flow paths for receiving adsorbent material therein for preferentially adsorbing a first gas component in response to increasing pressure in the flow paths relative to a second gas component. The function compartments include a gas feed compartment and a heavy product compartment.

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The feed gas to the hydrogen PSA system is reformat gas or syngas, generated in alternative fuel processing methods known to the art by steam reforming (e.g. of methanol or natural gas or light hydrocarbons), or by
5 autothermal reforming or partial oxidation (e.g. of natural gas, gasoline or diesel fuel). The CO content of methanol reformat (generated by relatively low temperature steam reforming of methanol) is typically about 1%. Other fuel processors (e.g. steam methane reformers, and POX or autothermal reformers operating on any feedstock) operate at much higher temperature, and preferably
10 include a lower temperature water gas shift reactor stage to reduce to CO content to about 1%.

The reformat gas contains hydrogen plus the basic impurity components of CO₂, CO and water vapour. If generated by air-blown POX or autothermal
15 reforming, the reformat gas will also contain a large inert fraction of nitrogen and argon. The fraction of inert atmospheric gases can be greatly reduced if an oxygen PSA system is used to supply the POX or autothermal reformer, either directly from the PSA, or as humid and still oxygen enriched air that has been passed through the fuel cell cathode channel which was directly fed oxygen-
20 enriched air from the PSA.

In one variation, the oxygen pressure swing adsorption system includes a compressor coupled to the gas feed compartment for delivering pressurized air to the gas feed compartment, and a vacuum pump coupled to the compressor for
25 extracting nitrogen product gas from the heavy product compartment. The reactor comprises a steam reformer, including a burner, for producing syngas, and a water gas shift reactor coupled to the steam reformer for converting the syngas to the second hydrogen gas feed. The hydrogen pressure swing adsorption system includes a vacuum pump for delivering fuel gas from the heavy product
30 compartment to the burner. The fuel gas is burned in the burner, and the heat generated therefrom is used to supply the endothermic heat of reaction necessary for the steam reformer reaction. The resulting syngas is delivered to the water gas

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shift reactor for removal of impurities, and then delivered as the second hydrogen gas feed to the hydrogen pressure swing adsorption system.

5 In another variation, the invention includes a burner for burning fuel. The reactor comprises an autothermal reformer for producing syngas, and a water gas shift reactor coupled to the autothermal reformer for converting the syngas to the second hydrogen gas feed. The compressor of the oxygen pressure swing adsorption system delivers pressurized air to the burner, and the heavy product gas is delivered from the hydrogen pressure swing adsorption system as tail gas to be
10 burned in the burner. The compression machine of the oxygen pressure swing adsorption system also includes an expander coupled to the compressor for driving the compressor from hot gas of combustion emitted from the burner. Heat from the burner may also be applied to preheat air and/or fuel supplied to the autothermal reformer.

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Independently of whether PSA is used for oxygen enrichment, the present invention provides a hydrogen PSA apparatus for purifying the reformat. The hydrogen PSA may be designed to deliver high purity hydrogen, or else may be designed less stringently to achieve adequately high removal of noxious
20 components (harmful to the fuel cell) such as CO, H₂S, halogens, methanol, etc. In the latter case, the hydrogen PSA would in its first pass only achieve partial removal of less harmful constituents (e.g., N₂, Ar and CO₂). In that case, anode tail gas would then preferably be recycled to the feed end of the PSA inlet for use in a feed pressurization step, thus avoiding any need for mechanical
25 recompression. Even when high hydrogen purity is specified for the PSA, this feature enables a small bleed from the end of the anode channel back to the feed pressurization step of the hydrogen PSA, as would be desirable for avoiding a strict dead-headed configuration with the risk of accumulation in the anode channel of any contaminant slip due to equipment imperfections or operational transient
30 upsets.

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Operating temperature of the adsorbers in the hydrogen PSA unit of the invention will preferably be elevated well above ambient, as the reformat gas is supplied at a temperature after water gas shift of typically about 200°C, while operating temperatures of PEM fuel cells may extend from 80°C to about 100°C.

5 Alternatively, the adsorbers may be operated at a lower temperature if the reformat is cooled, thus providing an opportunity for partial removal of water and any methanol vapour by condensation before admission to the hydrogen PSA unit. Advantages of operation at moderately elevated temperature are (1) reformat coolers and water condensers upstream of the hydrogen PSA can be avoided, (2)

10 PSA removal of water vapour and CO₂ may be more readily achieved at moderately elevated temperature compared to ambient temperature, (3) CO can be more selectively adsorbed than CO₂ over Cu(I) loaded adsorbents particularly at elevated temperature, and (4) kinetics of CO sorption and desorption on CO-selective sorbents will be greatly enhanced at higher temperature. Consequently a

15 preferred operating temperature range for the adsorbers is from about 80°C to about 200°C, and a more preferred operating range is from about 100°C to about 160°C.

The hydrogen PSA unit may be configured to support a temperature

20 gradient along the length of the flow channels, so that the temperature at the first end of the adsorbers is higher than the temperature at the second end of the adsorbers.

Especially in the mode of design for low purity hydrogen with anode

25 recycle, the hydrogen PSA may use CO-selective adsorbents with CO-complexing ions Cu(I) or Ag introduced by ion exchange or impregnation into a suitable adsorbent carrier. Prior art CO-selective adsorbents have used a wide diversity of zeolites, alumina or activated carbon adsorbents as carriers. With CO-selective adsorbents, enhanced hydrogen recovery may be achieved while tolerating some

30 accumulation of non-CO impurities circulated through the fuel cell anode loop.

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Numerous copper based CO-selective adsorbents have been disclosed by Rabo et al (U.S. Patent No.4,019,879), Hirai (U.S. Patent No.4,587,114), Nishida et al (U.S. Patent No. 4,743,276), Tajima et al (U.S. Patent No. 4,783,433), Tsuji et al (U.S. Patent No. 4,914,076), Xie et al (U.S. Patent No. 4,917,711),
5 Golden et al (U.S. Patent Nos. 5,126,310; 5,258,571; and 5,531,809), and Hable et al (U.S. Patent No. 6,060,032). Use of some such CO-selective adsorbents in pressure swing adsorption processes for removal or concentration of CO has been commercially established at industrial scale.

10 Use of some such adsorbents for removing CO from reformat for PEM fuel cells has been investigated by researchers at the Argonne National Laboratory, as reported in the 1998 annual report of the Fuel Cells for Transportation Program of the U.S. Department of Energy, Office of Advanced Transportation Technologies. Bellows (U.S. Patent No. 5,604,047) discloses use of selected
15 noble metals, and the carbides and nitrides of certain metals, as carbon monoxide adsorbents in a steam displacement purge cycle for removal of CO from reformat feed to fuel cells.

Potential problems with CO-selective adsorbents used to purify hydrogen
20 from reformat include (1) compatibility with water vapour that may deactivate the adsorbent or cause leaching of impregnated constituents, (2) over-reduction by hydrogen causing the CO-complexing ion to reduce to inert metallic form, and (3) relatively slow kinetics of CO-complexing as compared to physical adsorption.

25 In the present invention, the active adsorbent preferably including a CO-selective component is supported on thin adsorbent sheets which are layered and spaced apart by spacers defining flow channels, so as to provide a high surface area parallel passage support with minimal mass transfer resistance and flow channel pressure drop. With crystalline adsorbents such as zeolites, and
30 amorphous adsorbents such as alumina gel or silica gel, the adsorbent sheet is formed by coating or in-situ synthesis of the adsorbent on a reinforcement sheet of inert material, e.g. a wire mesh, a metal foil, a glass or mineral fiber paper, or a

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woven or nonwoven fabric. Active carbon adsorbent may also be coated onto a reinforcement sheet of inert material, but adsorbent sheets of active carbon may also be provided as self-supporting carbon fiber paper or cloth. Adsorbers of the layered adsorbent sheet material may be formed by stacking flat or curved sheets; or by forming a spiral roll, with the flow channels between the sheets extending from the first end of the adsorber to the second end thereof; to fill the volume of the adsorber housing of the desired shape. Typical thickness of the adsorbent sheet may be in the range of about 100 to about 200 microns, while flow channel spacing between the sheets may be in the range of about 50 to about 200 microns.

In the present invention, the adsorbent material contacting the flow channels between the first and second ends of the adsorbers may in general be selected to be different in distinct zones of the flow channels, so that the adsorbers would have a succession of zones (e.g. a first zone, a second zone, a third zone, a perhaps additional zones) with distinct adsorbents proceeding along the flow channels from the first end to the second end.

In a first variant configured to deliver high purity hydrogen, the adsorbent in a first zone of the adsorbers adjacent the first end will be a dessicant to achieve bulk removal of water vapour in that first zone, the adsorbent in a second zone in the central portion of the adsorbers will be selected to achieve bulk removal of CO₂ and some removal of CO, and the adsorbent in a third zone of the adsorbers will be selected to achieve final removal of CO and substantial removal of any nitrogen and argon. A suitable dessicant for the first zone is alumina gel. A suitable adsorbent for the second zone is 13X zeolite, or 5A, or active charcoal. Suitable adsorbents for the third zone may be a strongly carbon monoxide and nitrogen selective adsorbent selected from the group including but not limited to Na-LSX, Ca-LSX, Li-LSX, Li-exchanged chabazite, Ca-exchanged chabazite, Sr-exchanged chabazite. The zeolite adsorbents of this group are characterized by strong hydrophilicity, corresponding to selectivity for polar molecules. This first variant relying on physical adsorption will operate most effectively at relatively lower temperatures, unlikely to exceed much more than about 100°C

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although certain adsorbents such as Ca- or Sr-exchanged chabazite would remain adequately effective for CO and N₂ removal at temperatures to about 150°C.

5 In a second similar variant also configured to deliver high purity hydrogen, the adsorbent in the second or third zone may be a more strongly carbon monoxide selective adsorbent such as a Cu(I)-exchanged zeolite. The zeolite may for example be an X or a Y zeolite, mordenite, or chabazite. For stability against over-reduction while contacting nearly pure hydrogen, the exchangeable ions of the zeolite may be a mixture of Cu(I) and other ions such as Na, Li, Ca, Sr,
10 other transition group metals or lanthanide group metals. The mixed ions may also or alternatively include Ag as a minor component for enhanced CO-selectivity.

15 In a third variant configured to deliver at least partially purified hydrogen with CO nearly completely removed, the adsorbent in a first zone of the adsorbers adjacent the first end will be a dessicant to achieve bulk removal of water vapour in that first zone, the adsorbent in a second zone in the central portion of the adsorbers will be selected to achieve bulk removal of CO₂ and some removal of CO, and the adsorbent in a third zone of the adsorbers will be selected to achieve
20 final removal of CO and partial removal of any nitrogen and argon. A suitable dessicant for the first zone is alumina gel. A suitable adsorbent for the second zone is alumina gel impregnated with Cu(I), or active carbon impregnated with Cu(I). Suitable adsorbents for the third zone may be similar to those used in the second zone, or may be a CO- and nitrogen selective adsorbent as in the first or
25 second variants above.

In a fourth variant configured to deliver at least partially purified hydrogen with CO nearly completely removed, the adsorbent in some or all zones of the adsorbers will be a moderately hydrophobic adsorbent selected from the group
30 including but not limited to active carbon and Y-zeolite, and preferably containing Cu(I) for enhanced CO- selectivity in a zone adjacent the second end of the adsorbers.

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In a fifth variant configured to deliver at least partially purified hydrogen with CO nearly completely removed, the adsorbent in some or all zones of the adsorbers will be a strongly hydrophobic adsorbent selected from the group including but not limited to silicalite and dealuminified Y-zeolite. The hydrophobic adsorbent may preferably contain Cu(I) for enhanced CO- selectivity.

In a sixth variant configured to deliver at least partially purified hydrogen with CO nearly completely removed, the adsorbent in the first or second zone of the adsorbers will include a component catalytically active at the operating temperature of that zone for the water gas shift reaction. The catalytically active component may be any known water gas shift catalyst, e.g. Cu-ZnO based catalysts. Preferably, the catalytically active component may be metal carbonyl complexes of a transition group metal or a mixture of transition group metals (e.g. Cu, Ag, Ni, Pd, Pt, Rh, Ru, Fe, Mo, etc.) inserted into the zeolite cages of e.g. an X or Y zeolite. A portion of the carbon monoxide sorbed onto the catalytically active component may then react with water vapour by the water gas shift reaction to generate carbon dioxide and additional hydrogen. It is known [J.J. Verdonck, P.A. Jacobs, J.B. Uytterhoeven, "Catalysis by a Ruthenium Complex Heterogenized in Faujasite-type Zeolites: the Water Gas-shift Reaction", J.C.S. Chem. Comm., pp. 181-182, 1979] that ruthenium complexes stabilized within X or Y zeolites provide greater water-gas shift catalytic activity than conventional copper based catalysts.

In a seventh variant configured to deliver at least partially purified hydrogen with CO nearly completely removed, the adsorbent in the first zone of the adsorbers is an adsorbent selective at the elevated operating temperature of the first zone for carbon dioxide in preference to water vapour. Suitable such adsorbents known in the art include alumina impregnated with potassium carbonate, and hydrotalcite promoted with potassium carbonate. The adsorbent in the second zone of the adsorbers will include a component catalytically active at the operating temperature of that zone for the water gas shift reaction. As in the sixth variant above, the catalytically active component in the second zone may be

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a known water gas shift catalyst, or may be a transition group metal dispersed in zeolite cages and reversibly forming a metal carbonyl complex at the operating temperature of the second zone. The second or preferably third zone of the adsorbers contains adsorbent with some useful working capacity for carbon monoxide and other impurity components at the operating temperature of that zone. Because carbon dioxide is strongly adsorbed in the first zone, the concentration of carbon dioxide in the second zone is maintained at a reduced level by the PSA process, while water vapour concentration remains relatively high in the second zone. Hence, in this seventh variant the water gas shift reaction equilibrium is continually shifted by the PSA process which continually removes both hydrogen and carbon dioxide from the catalytically active second zone while preventing passage of carbon monoxide into the hydrogen product passing the third zone, so that essentially all carbon monoxide is consumed to generate carbon dioxide and additional hydrogen. This is an example of a PSA reactor or "sorption enhanced reactor", driving the water gas shift reaction substantially to completion while achieving adequate purification of the hydrogen.

Industrial H₂ PSA is normally conducted at considerably elevated pressures (> 10 bara) to achieve simultaneous high purity and high recovery (~ 80% - 85%). Fuel cell systems operating with pressurized methanol reformers or in integration with gas turbine cycles may operate at relatively high pressures. However, most PEM fuel cell systems operate at ambient to about 3 bara pressure. As feed pressure and the overall working pressure ratio of the PSA are reduced, productivity and recovery of a simple cycle deteriorate. Under given pressure conditions, use of CO-selective adsorbents should significantly improve recovery at specified product CO concentration, if hydrogen purity with respect to other impurities such as nitrogen and carbon dioxide can be relaxed.

At very low feed pressures (e.g. 2 - 3 bara), the H₂ PSA would need supplemental compression to achieve high recovery. We may consider vacuum pumping to widen the working pressure ratio, or alternatively "heavy reflux" which is recompression and recycle to the PSA feed of a fraction of its exhaust

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stream at full pressure. Vacuum and heavy reflux options may be combined in PSA systems for reformat purification. We have successfully used the heavy reflux option, without CO-selective adsorbents or any vacuum pumping, in a lab bench PSA device to achieve ~ 95% recovery from synthetic methanol reformat at ~3 bara feed pressure.

To get heavy reflux in a very low pressure PSA, the vacuum pump may be configured so that part of its flow is reinjected into the PSA feed. Extremely high hydrogen recovery can then be obtained (even at a fairly low overall pressure ratio) just by pumping enough heavy reflux. The vacuum level can be traded against the mass flow of heavy reflux.

A fuel cell may be a standalone power plant, or else it may be integrated with some type of combustion engine. In the case of a standalone fuel cell, all mechanical power for air handling compression and any oxygen and/or hydrogen PSA units must be provided as electrical power by the appropriately sized fuel cell stack. In this case, tight constraints apply to the recovery level that must be achieved by the H₂ PSA at specified purity. In the absence of any useful export use for high grade heat, an efficient heat balance requires that the heating value of combustible waste gases (H₂, CO and unreacted fuel) be matched to the heat demand of the fuel processor. For a fuel cell with steam reforming (e.g. methanol or natural gas), nominal hydrogen recovery by the H₂ PSA has to be about 75% to 80% as the PSA tail gas is burned to heat the reformer; while for a POX or autothermal reformer, hydrogen recovery by the PSA needs to be extremely high (at least 90% to 95%) as such reformers can only use a limited amount of external combustion heat from burning PSA tail gas or fuel cell anode tail gas, e.g. for preheating feed oxygen/air and fuel reactants to the reformer.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows an axial section of a rotary PSA module.

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Figs. 2 through 5B show transverse sections of the module of Fig. 1.

Fig. 6 is a simplified schematic of a PEM fuel cell power plant with a steam reforming fuel processor, a PSA unit for reformat hydrogen purification by at least removal of CO, and a VPSA unit for oxygen enrichment.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Figs. 1 - 5

Fig. 1 shows a rotary PSA module 1, which includes a number "N" of adsorbers 3 in adsorber housing body 4. Each adsorber has a first end 5 and a second end 6, with a flow path therebetween contacting a nitrogen-selective adsorbent. The adsorbers are deployed in an axisymmetric array about axis 7 of the adsorber housing body. The housing body 4 is in relative rotary motion about axis 7 with first and second functional bodies 8 and 9, being engaged across a first valve face 10 with the first functional body 8 to which feed gas mixture is supplied and from which the heavy product is withdrawn, and across a second valve face 11 with the second functional body 9 from which the light product is withdrawn.

In preferred embodiments as particularly depicted in Figs. 1 - 5, the adsorber housing 4 rotates and shall henceforth be referred to as the adsorber rotor 4, while the first and second functional bodies are stationary and together constitute a stator assembly 12 of the module. The first functional body shall henceforth be referred to as the first valve stator 8, and the second functional body shall henceforth be referred to as the second valve stator 9.

In the embodiment shown in Figs. 1 - 5, the flow path through the adsorbers is parallel to axis 7, so that the flow direction is axial, while the first and second valve faces are shown as flat annular discs normal to axis 7. However, more generally the flow direction in the adsorbers may be axial or radial, and the first and second valve faces may be any figure of revolution centred on axis 7. The steps of the process

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and the functional compartments to be defined will be in the same angular relationship regardless of a radial or axial flow direction in the adsorbers.

5 Figs. 2 - 5 are cross sections of module 1 in the planes defined by arrows 12 - 13, 14 - 15, and 16 - 17. Arrow 20 in each section shows the direction of rotation of the rotor 4. Fig. 2 shows section 12 - 13 across Fig.1, which crosses the adsorber rotor. In this example, "N" = 72. The adsorbers 3 are mounted between outer wall 21 and inner wall 22 of adsorber wheel 208. Each adsorber comprises a rectangular flat pack 3 of adsorbent sheets 23, with spacers 24 between the sheets to define flow
10 channels here in the axial direction. Separators 25 are provided between the adsorbers to fill void space and prevent leakage between the adsorbers. In other configurations, the adsorbent sheets may be formed in curved packs or spiral rolls.

Satisfactory adsorbent sheets have been made by coating a slurry of zeolite
15 crystals with binder constituents onto the reinforcement material, with successful examples including nonwoven fibreglass scrims, woven metal fabrics, and expanded aluminum foils. The adsorbent sheets comprise a reinforcement material, in preferred embodiments glass fibre, metal foil or wire mesh, to which the adsorbent material is attached with a suitable binder. For applications such as hydrogen purification, some
20 or all of the adsorbent material may be provided as carbon fibers, in woven or nonwoven form to serve as its own reinforcement material. Spacers are provided by printing or embossing the adsorbent sheet with a raised pattern, or by placing a fabricated spacer between adjacent pairs of adsorbent sheets. Alternative satisfactory spacers have been provided as woven metal screens, non-woven fibreglass scrims, and
25 metal foils with etched flow channels in a photolithographic pattern.

Typical experimental sheet thicknesses have been 150 microns, with spacer heights in the range of 100 to 150 microns, and adsorber flow channel length approximately 20 cm. Using X type zeolites, excellent performance has been achieved
30 in oxygen separation from air and hydrogen purification from reformat at PSA cycle frequencies in the range of 30 to 150 cycles per minute.

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As shown in Fig. 1, the adsorbers 3 comprise a plurality of distinct zones between the first end 5 and the second end 6 of the flow channels, here shown as three zones respectively a first zone 26 adjacent the first end 5, a second zone 27 in the middle of the adsorbers, and a third zone 28 adjacent the second end 6. The first zone typically contains an adsorbent or dessicant selected for removing very strongly adsorbed components of the feed gas mixture, such as water or methanol vapour, and some carbon dioxide. The second zone contains an adsorbent typically selected for bulk separation of impurities at relatively high concentration, and the third zone contains an adsorbent typically selected for polishing removal of impurities at relatively low concentration.

In embodiments with three zones, the first zone may be the first 10% to 20% of the flow channel length from the first end, the second zone may be the next roughly 40% to 50% of the channel length, and the third zone the remainder. In embodiments with only two adsorber zones, the first zone may be the first 10% to 30% of the flow channel length from the first end, and the second zone the remainder. The zones may be formed by coating the different adsorbents onto the adsorbent support sheet material in bands of the same width as the flow channel length of the corresponding zone. The adsorbent material composition may change abruptly at the zone boundary, or may be blended smoothly across the boundary. Particularly in the first zone of the adsorber, the adsorbent must be compatible with significant concentrations of water vapour.

For air separation to produce enriched oxygen, alumina gel may be used in the first zone to remove water vapour, while typical adsorbents in the second and third zones are X, A or chabazite type zeolites, typically exchanged with lithium, calcium, strontium, magnesium and/or other cations, and with optimized silicon/aluminum ratios as well known in the art. The zeolite crystals are bound with silica, clay and other binders, or self-bound, within the adsorbent sheet matrix.

In a first variant configured to deliver high purity hydrogen, the adsorbent in a first zone of the adsorbers adjacent the first end will be a dessicant to achieve

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bulk removal of water vapour in that first zone, the adsorbent in a second zone in the central portion of the adsorbers will be selected to achieve bulk removal of CO₂ and some removal of CO, and the adsorbent in a third zone of the adsorbers will be selected to achieve final removal of CO and substantial removal of any nitrogen and argon. A suitable dessicant for the first zone is alumina gel. A
5 Illustrative suitable adsorbents for the second zone are 13X zeolite, or 5A, or active charcoal. Suitable adsorbents for the third zone may be a strongly carbon monoxide and nitrogen selective adsorbent selected from the group including but not limited to Na-LSX, Ca-LSX, Li-LSX, Li- exchanged chabazite, Ca- exchanged
10 chabazite, Sr- exchanged chabazite. The zeolite adsorbents of this group are characterized by strong hydrophilicity, corresponding to selectivity for polar molecules. This first variant relying on physical adsorption will operate most effectively at relatively lower temperatures, unlikely to exceed much more than about 100°C although certain adsorbents such as Ca- or Sr-exchanged chabazite
15 remain adequately effective for CO and N₂ removal at temperatures up to about 150°C.

In a second similar variant also configured to deliver high purity hydrogen, the adsorbent in the second or third zone may be a more strongly carbon monoxide
20 selective adsorbent such as a Cu(I)-exchanged zeolite. The zeolite may for example be an X or a Y zeolite, mordenite, or chabazite. For stability against over-reduction while contacting nearly pure hydrogen, the exchangeable ions of the zeolite may be a mixture of Cu(I) and other ions such as Na, Li, Ca, Sr, other transition group metals or lanthanide group metals. The mixed ions may also or
25 alternatively include Ag(I) as a minor component for enhanced CO-selectivity.

In a third variant configured to deliver at least partially purified hydrogen with CO nearly completely removed, the adsorbent in a first zone of the adsorbers adjacent the first end will be a dessicant to achieve bulk removal of water vapour
30 in that first zone, the adsorbent in a second zone in the central portion of the adsorbers will be selected to achieve bulk removal of CO₂ and some removal of CO, and the adsorbent in a third zone of the adsorbers will be selected to achieve

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final removal of CO and partial removal of any nitrogen and argon. A suitable dessicant for the first zone is alumina gel. A suitable adsorbent for the second zone is alumina gel impregnated with Cu(I), or active carbon impregnated with Cu(I). Suitable adsorbents for the third zone may be similar to those used in the
5 second zone, or may be a CO- and nitrogen selective adsorbent as in the first or second variants above.

In a fourth variant configured to deliver at least partially purified hydrogen with CO nearly completely removed, the adsorbent in some or all zones of the
10 adsorbers will be a moderately hydrophobic adsorbent selected from the group including but not limited to active carbon and Y-zeolite, and preferably containing Cu(I) for enhanced CO- selectivity in a zone adjacent the second end of the adsorbers.

In a fifth variant configured to deliver at least partially purified hydrogen with CO nearly completely removed, the adsorbent in some or all zones of the
15 adsorbers will be a strongly hydrophobic adsorbent selected from the group including but not limited to silicalite and dealuminified Y-zeolite. The hydrophobic adsorbent may preferably contain Cu(I) for enhanced CO- selectivity.

In a sixth variant configured to deliver at least partially purified hydrogen with CO nearly completely removed, the adsorbent in the first or second zone of the adsorbers will include a component catalytically active at the operating
20 temperature of that zone for the water gas shift reaction. The catalytically active component may be any known water gas shift catalyst, e.g. Cu-ZnO based catalysts. Preferably, the catalytically active component may be metal carbonyl complexes of a transition group metal or a mixture of transition group metals (e.g. Cu, Ag, Ni, Pd, Pt, Rh, Ru, Fe, Mo, etc.) inserted into the zeolite cages of e.g. an X or Y zeolite. A portion of the carbon monoxide sorbed onto the catalytically
25 active component may then react with water vapour by the water gas shift reaction to generate carbon dioxide and additional hydrogen.
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In a seventh variant configured to deliver at least partially purified hydrogen with CO nearly completely removed, the adsorbent in the first zone of the adsorbers is an adsorbent selective at the elevated operating temperature of the first zone for carbon dioxide in preference to water vapour. Suitable such adsorbents known in the art include alumina impregnated with potassium carbonate, and hydrotalcite promoted with potassium carbonate. The adsorbent in the second zone of the adsorbers will include a component catalytically active at the operating temperature of that zone for the water gas shift reaction. As in the sixth variant above, the catalytically active component in the second zone may be a known water gas shift catalyst, or may be a transition group metal dispersed in zeolite cages and reversibly forming a metal carbonyl complex at the operating temperature of the second zone. The second or preferably third zone of the adsorbers contains adsorbent with some useful working capacity for carbon monoxide and other impurity components at the operating temperature of that zone. Because carbon dioxide is strongly adsorbed in the first zone, the concentration of carbon dioxide in the second zone is maintained at a reduced level by the PSA process, while water vapour concentration remains relatively high in the second zone. Hence, in this seventh variant the water gas shift reaction equilibrium is continually shifted by the PSA process which continually removes both hydrogen and carbon dioxide from the catalytically active second zone while preventing passage of carbon monoxide into the hydrogen product passing the third zone, so that essentially all carbon monoxide is consumed to generate carbon dioxide and additional hydrogen. The water gas shift reaction is thus driven substantially to completion, while achieving adequate purification of the hydrogen.

Fig. 3 shows the porting of rotor 4 in the first and second valve faces respectively in the planes defined by arrows 14 - 15, and 16 - 17. An adsorber port 30 provides fluid communication directly from the first or second end of each adsorber to respectively the first or second valve face.

Figs. 4A and 4B show the first stator valve face 100 of the first stator 8 in the first valve face 10, in the plane defined by arrows 14 - 15. Fluid connections are

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shown to a feed compressor 101 inducing feed gas from inlet filter 102, and to an exhauster 103 delivering second product to a second product delivery conduit 104. Compressor 101 and exhauster 103 are shown coupled to a drive motor 105.

5 Arrow 20 indicates the direction of rotation by the adsorber rotor. In the annular valve face between circumferential seals 106 and 107, the open area of first stator valve face 100 ported to the feed and exhaust compartments is indicated by clear angular segments 111 - 116 corresponding to the first functional ports communicating directly to functional compartments identified by the same reference numerals 111 -
10 116. The substantially closed area of valve face 100 between functional compartments is indicated by hatched sectors 118 and 119 which are slippers with zero clearance, or preferably a narrow clearance to reduce friction and wear without excessive leakage. Typical closed sector 118 provides a transition for an adsorber, between being open to compartment 114 and open to compartment 115. Gradual opening is provided by
15 a tapering clearance channel between the slipper and the sealing face, so as to achieve gentle pressure equalization of an adsorber being opened to a new compartment. Much wider closed sectors (e.g. 119) are provided to substantially close flow to or from one end of the adsorbers when pressurization or blowdown is being performed from the other end.

20 The feed compressor provides feed gas to feed pressurization compartments 111 and 112, and to feed production compartment 113. Compartments 111 and 112 have successively increasing working pressures, while compartment 113 is at the higher working pressure of the PSA cycle. Compressor 101 may thus be a multistage
25 or split stream compressor system delivering the appropriate volume of feed flow to each compartment so as to achieve the pressurization of adsorbers through the intermediate pressure levels of compartments 111 and 112, and then the final pressurization and production through compartment 113. A split stream compressor system may be provided in series as a multistage compressor with interstage delivery
30 ports; or as a plurality of compressors or compression cylinders in parallel, each delivering feed air to the working pressure of a compartment 111 to 113. Alternatively, compressor 101 may deliver all the feed gas to the higher pressure, with

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throttling of some of that gas to and 112 at their respective intermediate pressures.

Similarly, exhauster 103 exhausts heavy product gas from countercurrent
blowdown compartments 114 and 115 at the successively decreasing working pressures
of those compartments, and finally from exhaust compartment 116 which is at the
lower pressure of the cycle. Similarly to compressor 101, exhauster 103 may be
provided as a multistage or split stream machine, with stages in series or in parallel
to accept each flow at the appropriate intermediate pressure descending to the lower
pressure.

In the example embodiment of Fig. 4A, the lower pressure is ambient pressure,
so exhaust compartment 116 communicates directly to heavy product delivery conduit
104. Exhauster 103 thus is an expander which provides pressure letdown with energy
recovery to assist motor 105 from the countercurrent blowdown compartments 114
and 115. For simplicity, exhauster 103 may be replaced by throttling orifices as
countercurrent blowdown pressure letdown means from compartments 114 and 115.

In some preferred embodiments, the lower pressure of the PSA cycle is
subatmospheric. Exhauster 103 is then provided as a vacuum pump, as shown in Fig.
4B. Again, the vacuum pump may be multistage or split stream, with separate stages
in series or in parallel, to accept countercurrent blowdown streams exiting their
compartments at working pressures greater than the lower pressure which is the
deepest vacuum pressure. In Fig. 4B, the early countercurrent blowdown stream from
compartment 114 is released at ambient pressure directly to heavy product delivery
conduit 104. If for simplicity a single stage vacuum pump were used, the
countercurrent blowdown stream from compartment 115 would be throttled down to
the lower pressure over an orifice to join the stream from compartment 116 at the inlet
of the vacuum pump.

If the feed gas is provided at an elevated pressure at least equal to the higher
pressure of the PSA cycle, as may conveniently be the case of a hydrogen PSA
operating with e.g. methanol reformat feed, compressor 101 would be eliminated.

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To reduce energy losses from irreversible throttling over orifices to supply feed pressurization compartments e.g. 111, the number of feed pressurization stages may be reduced, so that adsorber repressurization is largely achieved by product pressurization, by backfill from light reflux steps. Alternatively, compressor 101 may be replaced in part by an expander which expands feed gas to a feed pressurization compartment e.g. 111 from the feed supply pressure of the higher pressure to the intermediate pressure of that compartment, so as to recover energy for driving a vacuum pump 103 which reduces the lower pressure below ambient pressure so as to enhance the PSA process performance.

Figs. 5A and 5B shows the second stator valve face, at section 16 - 17 of Fig. 1. Open ports of the valve face are second valve function ports communicating directly to a light product delivery compartment 121; a number of light reflux exit compartments 122, 123, 124 and 125; and the same number of light reflux return compartments 126, 127, 128 and 129 within the second stator. The second valve function ports are in the annular ring defined by circumferential seals 131 and 132. Each pair of light reflux exit and return compartments provides a stage of light reflux pressure letdown, respectively for the PSA process functions of supply to backfill, full or partial pressure equalization, and cocurrent blowdown to purge.

Illustrating the option of light reflux pressure letdown with energy recovery, a split stream light reflux expander 140 is shown in Figs. 1 and 5A to provide pressure let-down of four light reflux stages with energy recovery. The light reflux expander provides pressure let-down for each of four light reflux stages, respectively between light reflux exit and return compartments 122 and 129, 123 and 128, 124 and 127, and 125 and 126 as illustrated. The light reflux expander 140 may power a light product booster compressor 145 by drive shaft 146, which delivers the oxygen enriched light product to oxygen delivery conduit 147 and compressed to a delivery pressure above the higher pressure of the PSA cycle.

Since the light reflux and light product have approximately the same purity, expander 140 and light product compressor 145 may be hermetically enclosed in a

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single housing which may conveniently be integrated with the second stator as shown in Fig. 1. This configuration of a "turbocompressor" light product booster without a separate drive motor is advantageous, as a useful pressure boost of the light product can be achieved without an external motor and corresponding shaft seals, and can also be very compact when designed to operate at very high shaft speeds.

Fig. 5B shows the simpler alternative of using a throttle orifice 150 as the pressure letdown means for each of the light reflux stages.

Turning back to Fig. 1, compressed feed gas is supplied to compartment 113 as indicated by arrow 125, while heavy product is exhausted from compartment 117 as indicated by arrow 126. The rotor is supported by bearing 160 with shaft seal 161 on rotor drive shaft 162 in the first stator 8, which is integrally assembled with the first and second valve stators. The adsorber rotor is driven by motor 163 as rotor drive means.

As leakage across outer circumferential seal 131 on the second valve face 11 may compromise light product purity, and more importantly may allow ingress of humidity into the second ends of the adsorbers which could deactivate the nitrogen-selective or CO-selective adsorbent, a buffer seal 170 is provided to provide more positive sealing of a buffer chamber 171 between seals 131 and 171. Even though the working pressure in some zones of the second valve face may be subatmospheric (in the case that a vacuum pump is used as exhaustor 103), buffer chamber is filled with dry light product gas at a buffer pressure positively above ambient pressure. Hence, minor leakage of light product outward may take place, but humid feed gas may not leak into the buffer chamber. In order to further minimize leakage and to reduce seal frictional torque, buffer seal 171 seals on a sealing face 172 at a much smaller diameter than the diameter of circumferential seal 131. Buffer seal 170 seals between a rotor extension 175 of adsorber rotor 4 and the sealing face 172 on the second valve stator 9, with rotor extension 175 enveloping the rear portion of second valve stator 9 to form buffer chamber 171. A stator housing member 180 is provided as structural connection between first valve stator 8 and second valve stator 9.

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In the following figures of this disclosure, simplified diagrams will represent the PSA apparatus as described above. These highly simplified diagrams will indicate just a single feed conduit 181 to, and a single heavy product conduit 182 from, the first valve face 10; and the light product delivery conduit 147 and a single representative light reflux stage 184 with pressure let-down means communicating to the second valve face 11. Reference numerals pertaining to PSA units as described above will be unprimed for an oxygen enrichment PSA or VPSA unit, and primed for a hydrogen purification PSA or VPSA unit.

10 Fig. 6

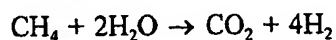
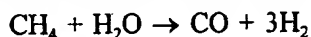
Fig. 6 shows a fuel cell power plant 200, according to the present invention, comprising a fuel cell 202, a steam reforming fuel processor 204, a hydrogen purification PSA system 205, and an oxygen enrichment VPSA system 206. The fuel cell comprises an anode channel 208 including an anode gas inlet 210 and an anode gas outlet 212, a cathode channel 214 including a cathode gas inlet 216 and a cathode gas outlet 218, and a PEM electrolyte membrane 220 cooperating with the anode channel 208 and the cathode channel 214 for facilitating ion exchange between the anode channel 208 and the cathode channel 214.

20 The oxygen VPSA system 206 extracts oxygen gas from feed air, and comprises a PSA rotary module 1 and a compressor 101 for delivering pressurized feed air to the feed compartments of the rotary module 1. The oxygen VPSA system 206 includes a vacuum pump 103 coupled to the compressor 101 for withdrawing nitrogen enriched gas as heavy product gas from the blowdown and exhaust compartments of the rotary module 1, and discharging the nitrogen enriched gas from conduit 225. The adsorbers 3 of rotary module 1 have a first zone 26 loaded with a suitable dessicant such as alumina gel for removal of water vapour, and a second zone 27 loaded with a nitrogen-selective zeolite. Dry oxygen enriched air as the light product gas of VPSA module 1 is delivered by conduit 147 to water management chamber 230 for humidification, and thence by conduit 231 to cathode inlet 216. A portion of the oxygen reacts with hydrogen ions when electric current is generated, to form water in the cathode. The cathode

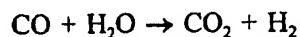
- 25 -

exhaust gas now containing a reduced amount of oxygen (but still typically oxygen-enriched well above ambient air composition) is withdrawn from cathode exit 218 by conduit 232. A portion of the cathode exhaust gas is removed from conduit 232 by conduit 233 and flow control valve 234, and may either be vented to atmosphere for purging nitrogen and argon accumulations, or else returned to the first valve face 10 of PSA module 1 as a feed pressurization stream at an intermediate pressure below the higher pressure of the PSA cycle. The remaining cathode exhaust gas is supplied to suction port 240 of an ejector 242 which serves as cathode gas recirculation means. The ejector receives enriched oxygen from conduit 147 through nozzle 244 which drives recirculation of cathode exhaust gas from suction port 240, and delivers the combined oxygen enriched gas stream to water management chamber 230 where excess water is condensed. The excess water is either exhausted through valve 250, or else is delivered as water reactant to fuel processor 204 by water pump 252 and conduit 254.

A hydrocarbon fuel is supplied to the fuel processor 204 by a feed pump or compressor 260, is combined with water from conduit 254, and is vaporized and preheated in heat exchanger 262. The preheated stream of fuel and steam is then admitted to steam reforming catalytic chamber 264, which is heated by burner 266 whose flue gas heats the heat exchanger 262. In the example that the fuel is methane, the following steam reforming reactions take place:



The resulting reformat or "syngas" (dry composition approximately 70% H_2 with roughly equal amounts of CO and CO_2 as major impurities, and unreacted CH_4 and N_2 as minor impurities) is cooled to about 250°C, and then passed to the water gas shift reaction zone 268 for reacting most of the CO with steam to produce more H_2 and CO_2 :



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The hydrogen rich reformat still contains about 1% to 2% CO after water gas shift, along with substantial amounts of carbon dioxide and water vapour. For high performance and longevity of a PEM fuel cell, it is necessary that CO concentration be reduced well below 100 ppm and preferably below 10 ppm.

5 Consequently, the impure reformat is admitted by conduit 270 to the higher pressure feed port of hydrogen PSA unit 205, including rotary PSA module 1'. The adsorbers 3' of rotary module 1' have a first zone 26' loaded with a suitable dessicant such as alumina gel for removal of water vapour, a second zone 27' loaded with an adsorbent selective for CO removal and at least partial bulk removal
10 of CO₂, and a third zone 28' loaded with an adsorbent suitable for polishing removal of CO and at least partial removal of other impurities such as N₂. The invention provides numerous combinations and variations of suitable adsorbents for the three zones of the hydrogen PSA adsorbers, as already recited above.

15 Purified hydrogen light product from the hydrogen PSA module 1' is delivered by conduit 147' to an ejector 242' which is recirculation means for partial recirculation of hydrogen rich anode gas through fuel cell anode channel 208. The hydrogen rich gas from ejector 242' is delivered to anode inlet 210, passed through anode channel 208, and then exhausted from anode exit 212 in part
20 back to the suction inlet of ejector 242'. Recirculation of anode gas through the ejector 242' is optional, so this ejector may be omitted. The remaining portion of the anode exhaust gas (or all of it in the case that ejector 242' is omitted) is conveyed by conduit 280 back to a feed pressurization port in the first valve surface 10' of hydrogen PSA module 1', so as to retain hydrogen within the system
25 while using the hydrogen PSA unit to reject impurities from the anode gas loop. A larger fraction of anode gas is recycled in this manner back to the PSA unit when adsorbent and PSA process combinations are selected that remove CO almost completely while allowing some passage of other impurities such as N₂ and perhaps some CO₂. Conversely, only a small amount of anode exhaust gas is
30 recycled back to the PSA to prevent inadvertent impurity accumulations, when the adsorbents and PSA cycle are designed to achieve high purity hydrogen with nearly complete removal of CO and other impurities as well.

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Exhaust second product gas from the hydrogen PSA module is exhausted from valve face 10' by conduit 285 to burner 266.

5 It will be understood by those skilled in the art that the hydrogen PSA unit of this invention, with the above specified combinations and variations of adsorbents in the sequential zones of the adsorbers, may be applied in conjunction with alternative fuel processors, including partial oxidation or autothermal reactors for processing of heavy as well as light hydrocarbon fuels to generate hydrogen
10 rich reformat, from which CO and other impurities must be removed.

Fig. 2

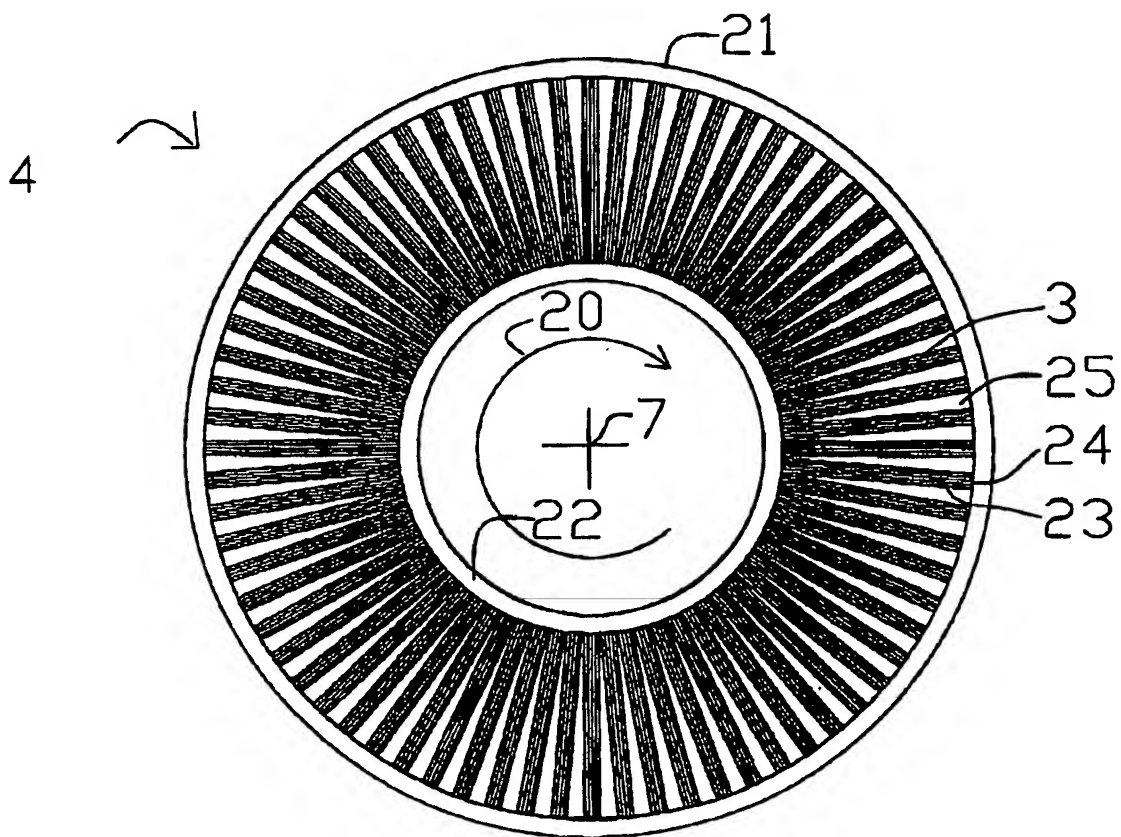


Fig. 3

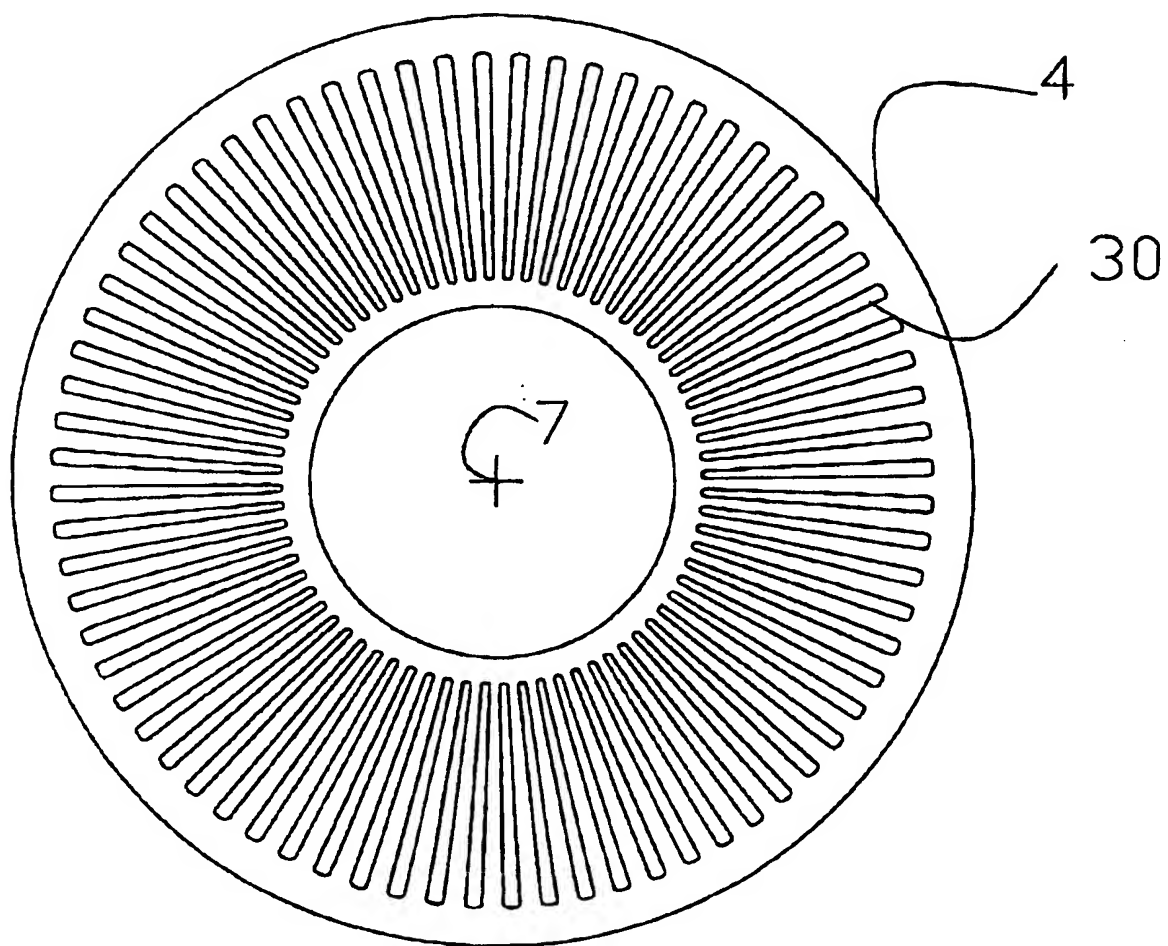


Fig. 4A

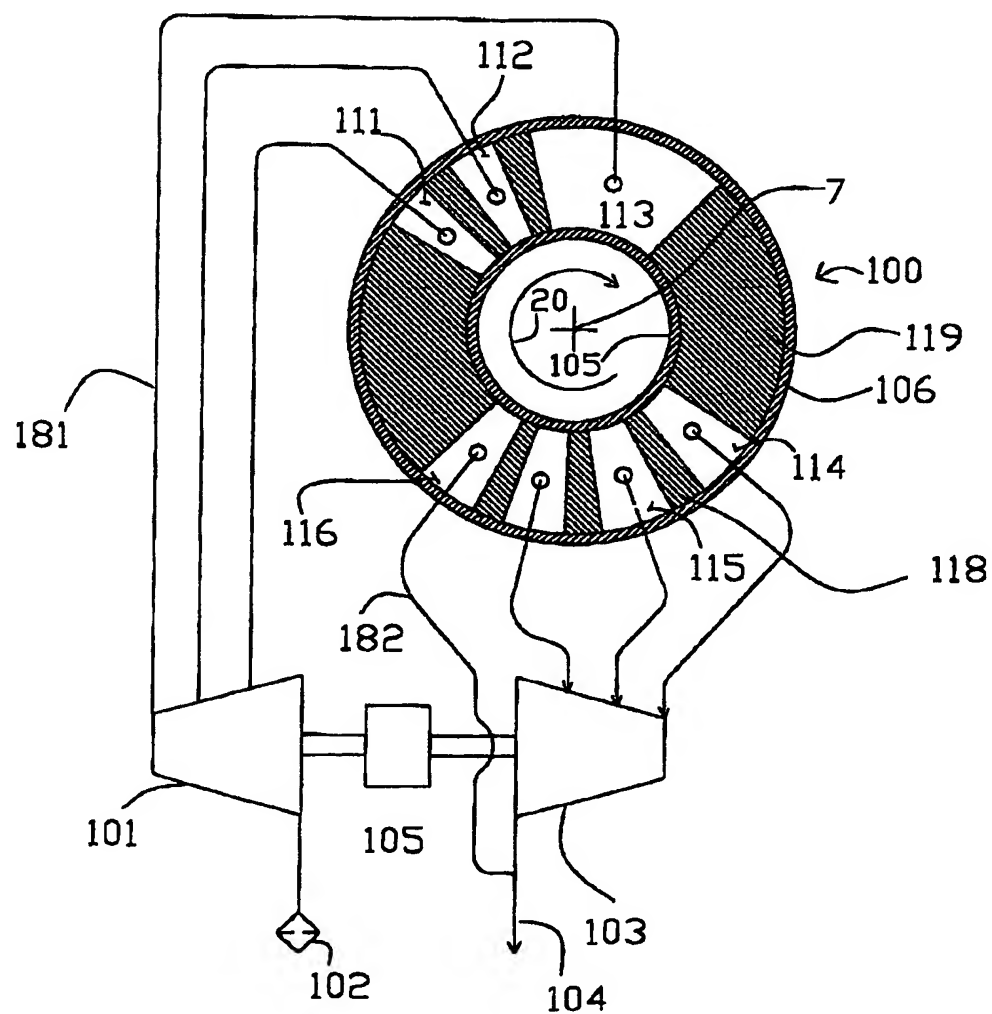


Fig. 4B

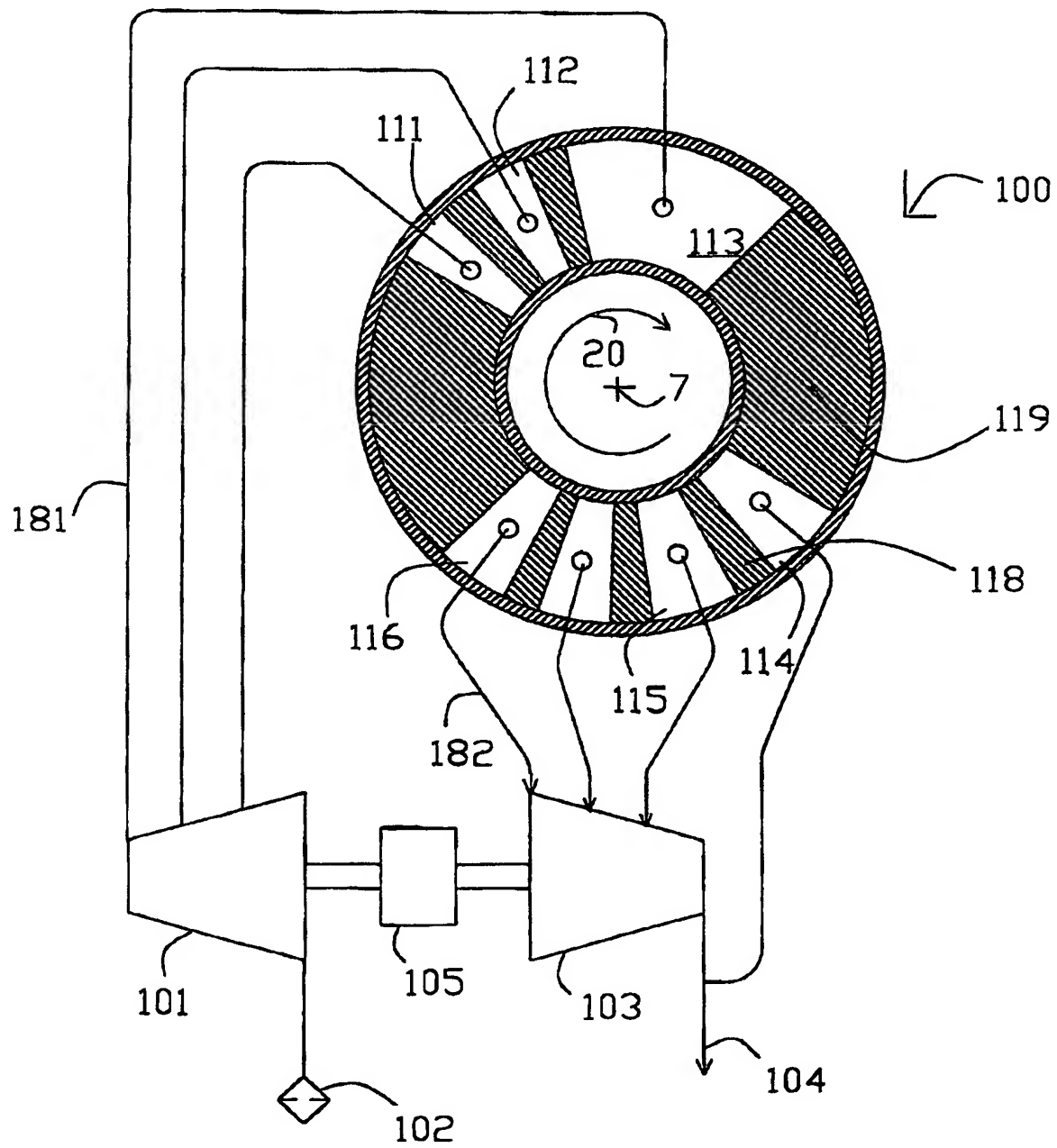


Fig. 5B

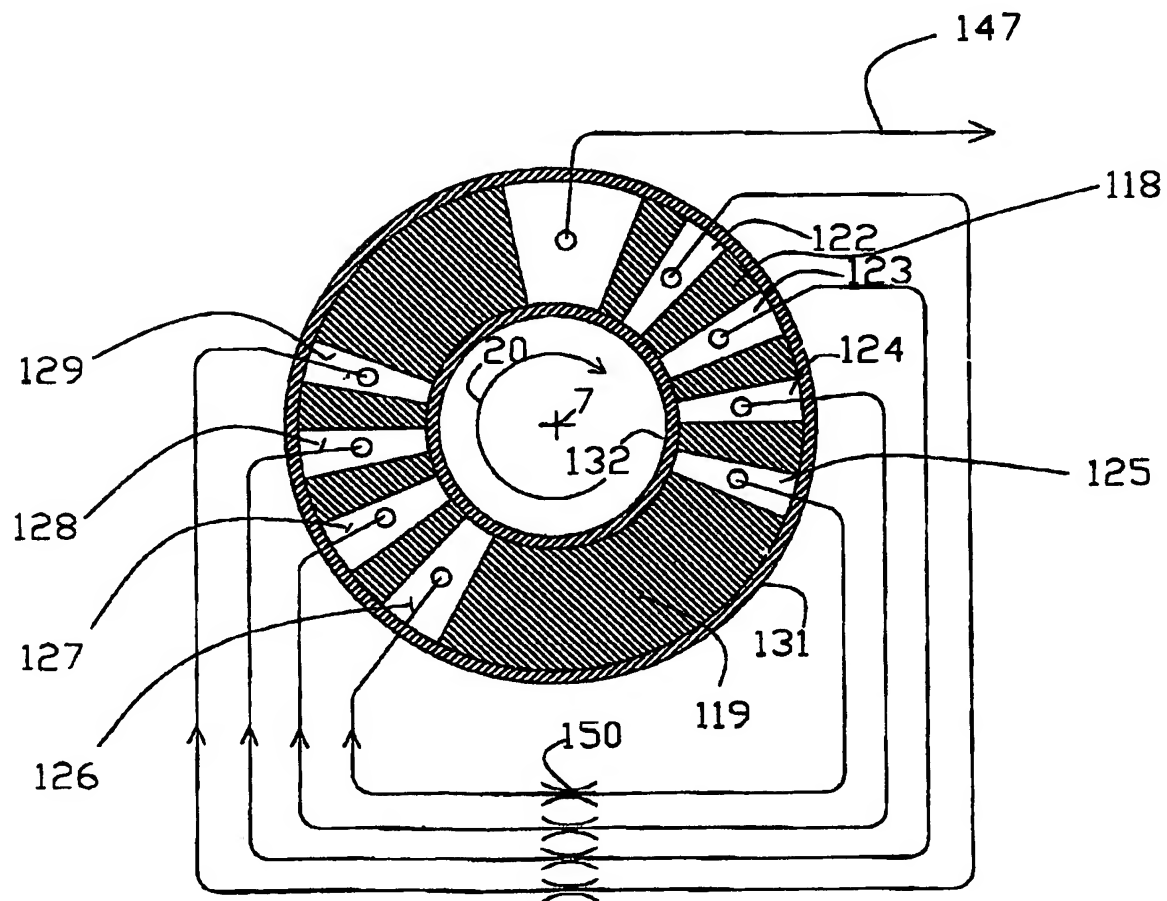


FIG. 6

